

Absorptions of Methyl and t-Butyl Halogenobenzoates in the Infrared Carbonyl Region

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Solutions of the methyl and t-butyl esters of *o*-, *m*-, and *p*-fluoro-, -chloro-, and -bromo-benzoates have been examined in the i.r. C=O region. All but one of the *o*- and *p*-esters show doublets whereas the *m*-isomers give single bands. The doublets of the *o*-esters arise from rotational isomers, the thermochemically less stable *syn-s-trans* forms absorbing at higher wavenumbers than the *anti-s-trans* rotamers: those of the *p*-isomers are caused by the operation of Fermi resonance. It is probable that the rotamers of the *m*-esters have similar C=O wavenumbers. A convenient, safe procedure for preparing t-butyl esters has been developed.

RECENT studies of compounds possessing a C=O group at position 2 of a heterocyclic system have shown that while ¹H n.m.r. spectroscopy is well suited to the investigation of rotational isomerism in aldehydes and methyl ketones,¹ esters are not amenable to this

detecting their rotational isomers.³ With some heterocyclic esters (especially those containing halogen substituents), the presence of two rotamers can be established most clearly by examining their i.r. C=O absorptions;² for the i.r. method to be valid, however, it

TABLE I

I.r. bands of alkyl halogenobenzoates in the C=O region

Solutions were examined as described previously² at a spectral slitwidth of 1.5 cm⁻¹. Band positions (at 303 K) are in cm⁻¹. Where two bands are shown the experimental trace was resolved into symmetrical components using an analogue computer; the components' positions are followed, in parentheses, by their percentage areas. Enthalpy differences (ΔH° /kJ mol⁻¹; statistical error ± 0.4 kJ mol⁻¹) between rotation isomers are in the direction (form with higher cm⁻¹) \rightarrow (form with lower cm⁻¹).

Ester	Fundamental region				Overtone region		ΔH° (in CCl ₄)
	CCl ₄		MeCN		CCl ₄		
(1a) R=Me	1 740 (40.5)	1 723.5 (59.5)	1 732.5 (59)	1 720 (41)	3 462 (38.5)	3 430 (61.5)	-1.9
(2a) R=But ^t *	1 730.5 (41)	1 710.5 (59)	1 723 (66)	1 707 (34)	3 443 (40)	3 404 (60)	-2.3
(1b)	1 742.5 (57.5) †	1 723.5 (42.5) †	1 737 (69)	1 723 (31)	3 464 (53)	3 434 (47)	-1.3
(2b)	1 731 (58.5) †	1 709.5 (41.5) †	1 720.5 (77) †	1 708 (23) †	3 444 (55)	3 401 (45)	-1.8
(1c)	1 741.5 (56.5)	1 725.5 (43.5)	1 735 (83)	1 721 (17)	3 465 (52)	3 432 (48)	-1.2
(2c)	1 732.5 (46.5)	1 713 (35.5)	1 728 (61)	1 710.5 (39)	3 442 (41)	3 408 (59)	-3.3
(1d)		1 731		1 726		3 447	
(2d)		1 720		1 713		3 442	
(1e)		1 733		1 726.5		3 448	
(2e)		1 719		1 713.5		3 419	
(1f)		1 732		1 726		3 446	
(2f)		1 720		1 713.5		3 421	
(1g)	1 729 (82)	1 720 (18)		1 723 §		3 440	
(2g)	1 720 (20) †	1 715 (80) †	1 726 (18)	1 709 (82)		3 415	
(1h)		1 729		1 724		3 440	
(2h)	1 726 (25.5) †	1 716.5 (74.5) †	1 725.5 (11)	1 712.5 (89)		3 437	
(1i)	1 731 (80.5) †	1 716.5 (19.5) †	1 725.5 (84.5)	1 715.5 (15.5)		3 440	
(2i)	1 723.5 (23.5)	1 715.5 (76.5)	1 723 (7)	1 711 (93)		3 418	

* Table 2. † As in previous work,² *syn* and *anti* refer to the relative dispositions of the carbonyl oxygen and the halogen atoms; *trans* describes the arrangement of the alkyl and aryl groups about the formal C-O single bond. ‡ A third (weak) band is needed to optimise the fit to the experimental trace. § Broad band.

* Ref. 10.

approach.² Further, the lower barrier to rotation of the esters reduces the effectiveness of ¹³C n.m.r. in

¹ B. P. Roques and S. Combrisson, *Canad. J. Chem.*, 1973, **51**, 573; R. J. Abraham and T. M. Siverns, *Tetrahedron*, 1972, **28**, 3015 and earlier papers cited there.

² D. J. Chadwick, J. Chambers, R. Macrae, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, 1976, 597; D. J. Chadwick, J. Chambers, G. D. Meakins, S. E. Musgrave, and R. L. Snowden, *J. Chem. Research (S)*, 1977, 26.

is essential to adopt systematic approaches in distinguishing between various possible causes of multiple absorption in the C=O region.⁴

With the esters of halogenobenzoates there appears to

³ D. J. Chadwick, G. D. Meakins, and E. E. Richards, *Tetrahedron Letters*, 1974, 3183.

⁴ D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, 1975, 13.

have been little i.r. work other than the original investigation of methyl esters,⁵ and, not surprisingly, no n.m.r. studies concerned with the occurrence of rotational isomerism. Since the i.r. examination⁵ did not reveal certain features needed to establish unequivocally the origin of the band splitting observed in many of the esters, a systematic investigation of the methyl and t-butyl esters of nine halogenobenzoic acids was undertaken.

The main findings are shown in Table 1; details of the variable temperature and concentration experiments are recorded for one ester (Table 3, Experimental section). For i.r. characteristics common to the two investigations (*e.g.*, band positions of solutions in CCl₄) there is excellent agreement between the previous⁵ and the present values.

TABLE 2
Characterisation of t-butyl esters

t-Butyl	B.p. (°C) [<i>p</i> /mmHg]	Analytical figures (%)	C H Hal		
			C	H	Hal
<i>o</i> -Fluorobenzoate (2a)	78—79 [0.4]	Found C ₁₁ H ₁₃ FO ₂ requires	67.2 67.3	6.9 6.7	9.8 9.7
<i>o</i> -Chlorobenzoate (2b)	96—97 [0.2]	Found C ₁₁ H ₁₃ ClO ₂ requires	62.3 62.1	6.2 6.2	16.5 16.7
<i>o</i> -Bromobenzoate (2c)	132—133 [1.2]	Found C ₁₁ H ₁₃ BrO ₂ requires	51.7 51.4	4.8 5.1	30.9 31.1
<i>m</i> -Fluorobenzoate (2d) *	50—51 [0.3] †	Found	67.1	6.7	9.6
<i>m</i> -Chlorobenzoate (2e)	133—134 [21]	Found	61.8	6.0	17.0
<i>m</i> -Bromobenzoate (2f)	81—83 [0.2]	Found	51.7	5.2	30.0
<i>p</i> -Fluorobenzoate (2g)	51—52 [0.4]	Found	67.1	6.8	9.5
<i>p</i> -Chlorobenzoate (2h) *	109—110 [12] ‡	Found	62.4	6.1	16.9
<i>p</i> -Bromobenzoate (2i) §	81—82 [0.8]	Found	51.6	5.4	30.8

* Prepared previously (ArCOCl—Bu^tOH—C₆H₅N) by G. G. Smith and B. L. Yates (*Canad. J. Chem.*, 1965, **43**, 702).
† B.p. 62—63° at 0.6 mmHg. ‡ B.p. 94° at 0.33 mmHg.
§ B. F. Hofferth, *Iowa State College Journal of Science*, 1957, **26**, 219, gives b.p. 138—139° at 12 mmHg.

Consideration of the results obtained with the *o*-esters (1a—c) and (2a—c) along the lines discussed fully in earlier work^{2,4} leaves no doubt that these esters exhibit rotational isomerism, the higher and the lower wavenumber components of the carbonyl doublets arising from the *syn-s-trans* and the *anti-s-trans* forms respectively. (The depictions of these forms in Table 1 are not intended to imply coplanarity of the ester groups and the aromatic rings; indeed, recent studies⁶ of halogen-substituted benzaldehydes and acetophenones suggest that the dihedral angles are probably >20°). The presence of single C=O bands in the spectra of the

⁵ C. J. W. Brooks, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 1961, 106.

⁶ C. L. Chang, R. J. W. Le Fevre, G. L. D. Ritchie, P. A. Goodman, and P. H. Gore, *J. Chem. Soc. (B)*, 1971, 1198; E. A. W. Bruce, G. L. D. Ritchie, and A. J. Williams, *Austral. J. Chem.*, 1974, **27**, 1809; C. T. Aw, H. H. Huang, and E. L. K. Tan, *J.C.S. Perkin II*, 1972, 1638; M. G. Belsham, A. R. Muir, M. Kinns, L. Phillips, and Li-Ming Twanmoh, *ibid.*, 1974, 119; T. Drakenberg, R. Jost, and J. M. Sommer, *ibid.*, 1975, 1682.

m-esters does not imply that they adopt one preferred conformation. It is more probable that the single bands represent closely overlapping absorptions from appreciable amounts of both rotamers. [Dipole moment studies of methyl *m*-chlorobenzoate in non-polar solvents⁷ indicate an equilibrium between *syn* (*ca.* 44%) and *anti* forms (*ca.* 56%).] The components of the doublets observed with five of the six *p*-esters are less well separated than those of the *o*-isomers' doublets. Rotational isomerism cannot be the cause of the *p*-esters' doublets, and the variable temperature examinations exclude the possibility that they arise consistently from hot transitions. The results in Table 1 establish that the multiple absorptions of the *p*-esters originate in Fermi resonance.

This work emphasises the need for caution in associating a doublet C=O absorption with the presence of rotational isomers. Variable temperature examination is useful in that a Fermi resonance doublet may give an unacceptably high supposed 'enthalpy difference', for example, a value of *ca.* 7 kJ mol⁻¹ for methyl *p*-chlorobenzoate in CCl₄.

EXPERIMENTAL

Preparation of t-butyl esters from acid chlorides and t-butyl alcohol in pyridine is generally less satisfactory than that employing the acid and 2-methylpropene.⁸ In the present work the procedure for carrying out the latter method in a glass apparatus⁹ was found to lead to explosions in some preparations; the modified technique of using a steel vessel as described here is safe, convenient, and efficient.

Esters.—Commercially available halogenobenzoic acids were converted into methyl esters as described previously,⁷ and into t-butyl esters by the following procedure. A stainless steel sampling cylinder (Hone Instruments; 200 ml; capped at both ends by screw-in Monel plugs fitted

TABLE 3

C=O Bands of methyl *o*-fluorobenzoate in CCl₄. The statements at the head of Table 1 apply here also. Concentrations (*c*) are in mg per g of solvent

<i>T</i> /K	<i>c</i>	Positions and areas of bands	
258	1.45	1 736.5 (38)	1 720 (62)
276	1.45	1 737.5 (37.5)	1 721.5 (59.5)
288	1.45	1 739 (38)	1 722.5 (57)
303	1.45	1 740 (38)	1 723.5 (54.5)
318	1.45	1 741 (36)	1 724.5 (51.5)
333	1.45	1 742 (36)	1 725 (49.5)
348	1.45	1 742.5 (36)	1 725.5 (46.5)
Variable concentration			
303	15.5	1 739.5 (43)	1 723 (57)
303	1.45	1 740 (41)	1 723.5 (59)
303	0.141	1 740 (42)	1 723.5 (58)

with vacuum seals) in an upright position and with one cap removed was cooled to -40 °C with the open end of the cylinder protruding from the coolant. The carboxylic acid (2 g) was suspended or dissolved in dry Et₂O (60 ml)—H₂SO₄

⁷ R. A. Y. Jones, A. R. Katritzky, and A. V. Ochkin, *J. Chem. Soc. (B)*, 1971, 1795.

⁸ R. Altschul, *J. Amer. Chem. Soc.*, 1946, **68**, 2605.

⁹ D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, 1973, 1776.

(3 ml); $\text{Me}_2\text{C}:\text{CH}_2$ (40 ml) and eight stainless steel balls (diameter *ca.* 1 cm) were added, and the cap was replaced. The cylinder, attached by a cradle around the middle of its length to a disc on the shaft of a stirrer motor, was rotated at such a speed (*ca.* 40 r.p.m.) that the balls ran along the cylinder during each half revolution. After 1 day the cylinder was cooled to -40°C and opened, and the contents were poured slowly, with stirring, into aqueous 5% KOH (200 ml) at 5°C . The Et_2O layer was washed with water, dried, filtered through a column of SiO_2 (50 g), and evaporated to give the t-butyl ester (2—2.5 g).

Each ester was distilled *in vacuo* immediately before i.r. examination, and shown to give one peak on g.l.c. (Pye Argon Chromatograph; 1 m column of 10% polypropylene

adipate on Embacel; 125°C ; argon pressure 10 lb in^{-2}). The b.p.s of the methyl esters agreed with the literature values. The characterisation of the t-butyl esters is shown in Table 2.

I.r. Work.—Spectra were recorded as described previously,¹⁰ and a Dupont 310 Curve Resolver was used to separate overlapping bands. Table 3 illustrates the results obtained in variable temperature and concentration experiments.

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¹⁰ D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J.C.S. Perkin II*, 1972, 1959; 1976, 1.
